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Precipitation and Inactivation of Phosphorus as a Lake Restoration Technique

Kent State Univ., OH

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PRECIPITATION AND INACTIVATION OF PHOSPHORUS AS A LAKE RESTORATION TECHNIQUE

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ABSTRACT

Many eutrophic lakes respond slowly following nutrient diversion because of long water retention times, and the recycling of phosphorus from sediments and other internal sources. Treatment of lakes with aluminum sulfate and/or sodium aluminate is a successful method for removing phosphorus from the water column and for controlling its release from sediments. Twenty-eight lake projects treated with aluminum salts are reviewed and summarized. The technique is successful when sufficient doses of aluminum are applied, however a few undesirable side-effects such as reduced planktonic microcrustacea species diversity and increases in rooted plant biomass may occur. Two methods for determining aluminum sulfate doses are compared. Both approaches are related directly to treatment objectives and involve simple laboratory methods. One approach emphasizes short-term reductions in water column phosphorus concentration. The other emphasizes long-term control of sediment phosphorus release while also assuring maximum removal of phosphorus from the water column at the time of treatment. Maximum dose, dictated by the buffering capacity of the particular lake, is defined as that dose which reduces pH to 6, a pH favorable for forming insoluble aluminum hydroxide and for assuring that dissolved aluminum remains below potentially toxic concentrations. Lake dosage can be easily determined prior to application by titrating several lake water samples of varying alkalinity with aluminum sulfate, determining maximum dose for each sample, and establishing a relationship between alkalinity and maximum dose. This lake restoration technique is successful and long-lasting when properly applied. It would become a standard means of treating small lakes or ponds following diversion. Additional efforts should be directed toward long term monitoring of selected projects, studies of application methods and the potential toxicity of chemically treating lakes.

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I. Introduction

Nutrient diversion alone does not always bring about prompt and sufficient reduction in lake water concentration due to recycling from nutrient-rich sediments (Larsen et al., 1975; Cooke et al., 1977). Certain lakes continue to have nuisance algal blooms and require an additional restorative steps. The phosphorus (P) precipitation/inactivation technique is a procedure to remove P from the water column and to control its release from sediments in order to achieve P-limiting conditions to algal growth following nutrient diversion.

The salts of iron, aluminum, and other metals have long been used in advanced wastewater treatment to remove P and this technology was extended to lake rehabilitation. Iron (Fe III) was apparently first used at Dorrdrecht Reservoir (Netherlands) in 1962 (Peelen, 1969) and the first use of aluminum sulfate to precipitate P from the water column at Lake Langsjon, Sweden, in 1968 (Jernelov, 1970). Since those early lake treatments, considerable advances in our knowledge of dose, effectiveness, costs, side-effects and other factors have occurred. The purpose of this paper is to describe the current state-of-the-art of this lake rehabilitation technique.

II. The Chemistry of Phosphorus Inactivants/Precipitants

The chemical and physical bases for the use of phosphorus precipitants/inactivants is their ability to form complexes, chelates, and insoluble precipitates with phosphorus. Iron and calcium have distinct disadvantages in this regard. During spring and fall circulation, or just after thermal stratification, lake sediments are covered by an oxidized microzone which traps P by precipitation with hydrated iron oxides. As the dissolved oxygen content of the hypolimnion falls, the redox potential also decreases and P is released during the reduction of ferric hydroxide and other iron complexes. Thus iron is not a suitable inactivant for long-term control of P release. This relationship of iron, phosphorus, and redox is summarized by Morgan and Stumm (1964) and Stumm and Morgan (1970). Calcium additions to lakes may lead to the formation of apatite and hydroxylapatite, but effective P removal occurs at pH values above those those found in natural waters (Stumm and Morgan, 1970; Wetzel, 1975), and thus addition of lime (CaO) for P removal may induce damage to the biota.

Aluminum has been used most often in P inactivation/precipitation projects because Al complexes and polymers are inert to redox changes, are effective in entrapment and removal of inorganic and particulate P in the water column when given sufficient contact time, and are apparently of low toxicity at the pH and dose required to bring about lake improvement. The most common forms of aluminum used are aluminum sulfate (alum) and sodium aluminate, both of which produce aluminum hydroxide in aqueous solution. The floc of aluminum hydroxide, once deposited, seems to "consolidate" with the sediments within weeks (Cooke et al., 1978). Phosphorus-rich water, including interstitial water and groundwater, are presumably stripped of P as they move through the floc.

Aluminum hydroxide, which is formed when aluminum salts are added to water is unique among nontransition metal hydroxides in that it is amphoteric, forms complex ions with other substances commonly found in natural waters, and polymerizes (Burrows, 1977). It is these properties which have made aluminum a valuable agent for the treatment of water and wastes.

The dissolution of aluminum salts in pure water brings about the coordination of six water molecules to form a hydrated trivalent aluminum ion (Fiat and Connick, 1968). This ion then undergoes a series of pH dependent hydrolysis reactions ultimately forming colloidal aluminum hydroxide:

$$Al^{+3} + 6H_2O \rightleftarrows Al(H_2O)_6^{+3} \qquad (1)$$

$$Al(H_2O)_6^{+3} + H_2O \rightleftarrows Al(H_2O)_5O^{+2} + H^+ \qquad (2)$$

etc.

$$Al(OH)^{+2} + H_2O \rightleftarrows Al(OH)_2 + H^+ \qquad (3)$$

$$Al(OH)_2^{+} + H_2O \rightleftarrows Al(OH)_3 + H^+ \qquad (4)$$

The result is a decrease in solution pH, and in natura. waters, a decrease in total alkalinity.

Aluminum hydroxide, because of its amphoteric property, is converted to the soluble aluminate ion in basic solutions:

$$Al(OH)_3 + H_2O \rightleftarrows Al(OH)_4^- + H^+ \qquad (5)$$

The distribution of hydrolyzed aluminum species is dependent on solution pH (Figure 1), with settleable, polymerized $Al(OH)_3$ predominating between pH 6 and 8. The formation of aluminate ion is favored above this range, while Al^{+3} predominates below pH 4. A number of other hydrolysis species have been postulated and the reader should consult such reviews as that of Hayden and Rubin (1974) for more complete discussions of the hydrolysis of aluminum.

Removal of P by aluminum can occur by precipitation of $AlPO_4$ (Recht and Ghassemi, 1970), sorption of phosphates to the surface of aluminum hydroxide polymers or floc (Eisenreich et al., 1977), and/or by entrapment/sedimentation of P-containing particulates by aluminum hydroxide floc. The dominant mechanism(s) for removal will depend on chemical and physical conditions under which treatment occurs and the nature of the P species present.

The removal of inorganic P is dependent primarily on reaction pH and P concentration. In general, high inorganic P concentrations (> 1 mg P/l), such as those encountered during wastewater treatment, and low pH would favor the formation of $AlPO_4$. Theoretically, under these conditions and in the presence of excess P, the removal of one mole of P as $AlPO_4$ would require one mole of aluminum. However, Al/P molar ratios for maximal removal during conventional wastewater treatment are often greater than unity. For example, Linsted et al. (1974) achieved maximal P removal from sewage at pH 5-6 using a treatment Al/P molar ratio of 2.3.

At lower inorganic P concentrations (< 1 mg P/l) and higher pH, OH^- competes with PO_4^{-3} for aluminum ions (Hsu, 1976), favoring the formation of aluminum hydroxide-phosphates. Under these conditions, maximal P removal efficiencies occur at even higher Al/P molar ratios. Maximum P removal from Cline's Pond water (0.43 mg P/l iniital soluble reactive P concentration), which was found to be pH dependent, occurred at Al/P molar ratios ranging from 5.7 to 7.2 (S. A. Peterson et al., 1976). Al/P molar ratios in excess of 525 were required to achieve 90 percent P removal from ulfiltered Lake Mendota epilimnetic water (0.01 mg P/l initial soluble reactive P concentration) at pH 6.5 to 7.0 (Eisenreich et al., 1977).

Dissolved organic phosphates are removed considerably less effectively due presumably to their complex molecular structure and chemical characteristics (Browman et al., 1973, 1977; Eisenreich et al., 1977). The effeciency of removal appears to be related more to the types of organic phosphates present than to treatment conditions. If the objective of an alum application is to reduce P to limiting concentrations, as would be the case for lake treatments, failure to remove dissolved organic P could be of significance

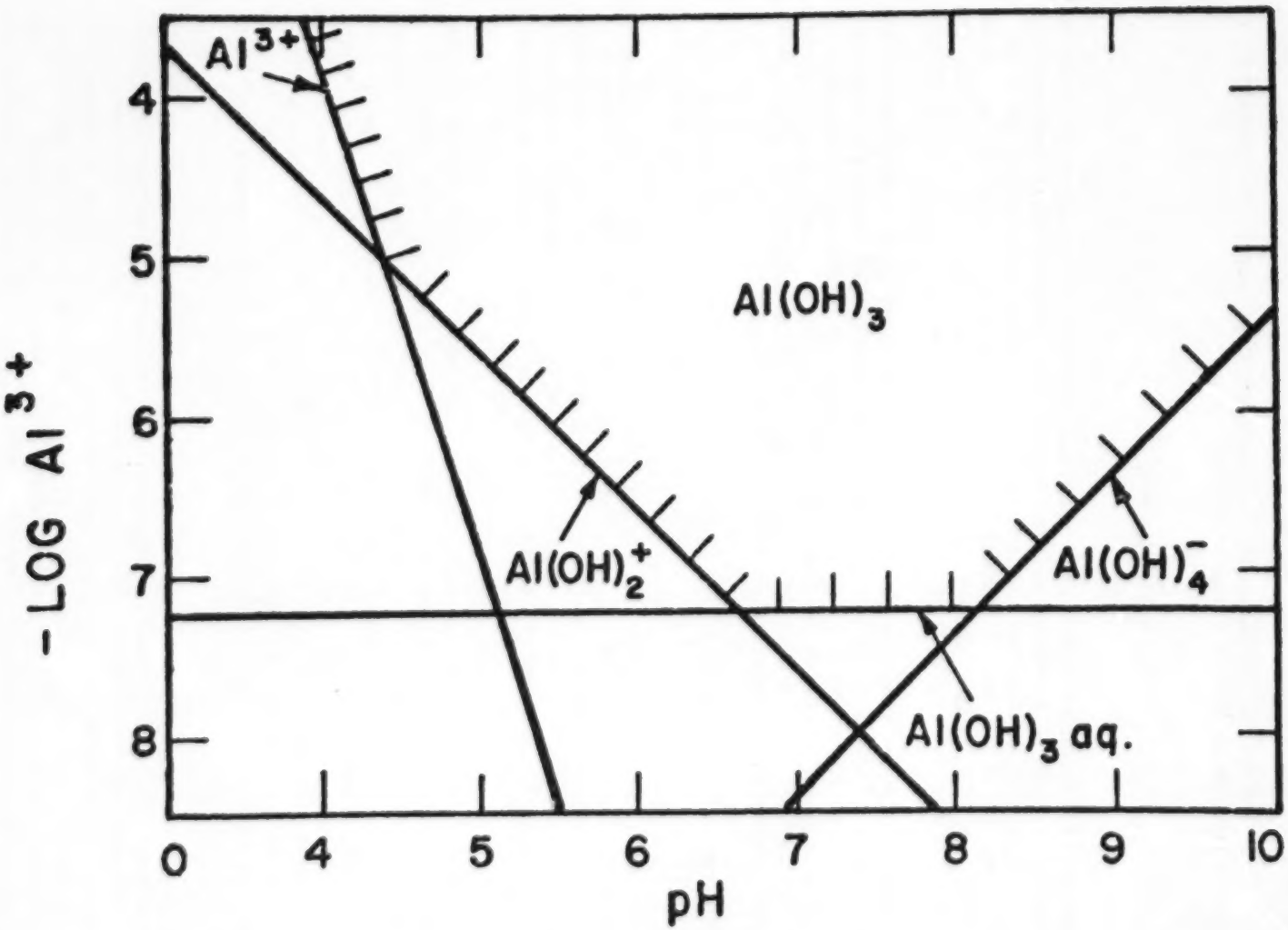


Figure 1. Solubility of amorphous hydroxide (from Eisenreich et al., 1977 as adopted from Anderson and Arledge, 1962).

since it has been shown that certain nuisance blue-green algae, under P-limiting conditions, will produce an enzyme (phosphatase) which will remove inorganic P from any organic phosphates at rates sufficient to support algal blooms (Heath and Cooke, 1975).

Effective removal of particulate P depends on both the quantity and quality of aluminum hydroxide floc produced during treatment. As indicated above, aluminum solubility is pH dependent with maximum floc formation occurring at approximately pH 6 to 8. Therefore, it would be expected that the potential for entrapment of particulates would be greatest within this range. Recht and Ghassemi (1970) observed maximal floc formation in the range pH 5-7. Similar results have also been obtained for mineral suspensions with the greatest reduction in turbidity occurring in the range pH 6.8 to 7.8 (Packham, 1962). Outside of the range of minimum solubility, dissolved aluminum concentrations increase, floc size and quantity decrease, and settleability is reduced. Therefore, with pH controlled, particulate removal rates are then dose dependent.

The amount of alum added to lakes and the manner in which it is applied will have a marked effect on the chemical conditions at the time of treatment. These conditions, particularly pH, will in turn influence the effectiveness of P removal and dictate the mechanism by which it occurs. As will be discussed in a subsequent section ("Dose Determination"), dosages sufficient to reduce pH to approximately 6.0 will result in maximum P removal (primarily by sorption to particulate aluminum hydroxide floc) but more importantly, provide for a maximum addition of aluminum to sediments.

Once deposited, aluminum hydroxide provides continued P control. Kennedy (1978) monitored P concentrations in experimental enclosures above alum-treated and untreated sediments and determined that treated sediments were active in retaining P. Conditions at the sediment/water interface (i.e., low pH and high P concentrations) will favor the formation of $AlPO_4$. Laboratory elution experiments (Kennedy, 1978) using pre-formed floc provide data suggesting that such formation occurs at molar ratios between 2 and 4. Therefore, the P-trapping effectiveness of the floc layer will depend on the amount of aluminum present, pH, the concentration of P and the rate at which P is supplied to the floc surface.

III. Criteria for Successful Lake Treatment

No common set of procedures, dose determinations, and matters related to application has emerged from the several field tests of the P precipitation/inactivation technique. The following factors must be considered; 1) dose; 2) choice of dry of liquid chemical; 3) depth of application; 4) application procedures; 5) season; 6) side-effects; and 7) lake types best suited for the technique. Definite statements about these factors cannot always be given, due in part to an absence of information, but also because the user will have to evaluate the individual situation, the objective of the treatment, and varying social-economic factors of importance. The following is a summary of current knowledge and experience of those who have worked with the technique.

1. Dose Determination

An objective of all alum treatments is the control of P release from bottom sedmients. However, in early treatments this was often considered to be secondary to P removal from the water column (e g., J. O. Peterson et al., 1973; S. A. Peterson et al., 1974). More recently, lake treatments have been conducted with control of P release from sediments as the stated primary objective (e.g., Cooke et al., 1978; Kennedy, 1978). Two different approaches to dose determination, both related directly to treatment objective, have been followed. In the first, dosage is optimized for P removal from the water column with little attention given to the quantity of floc ultimately deposited on bottom sediments. Dose is determined by jar tests in which aluminum salts are added until a desired P removal is achieved. This laboratory determined dose is then used directly to calculate dose on a lake volume basis (e.g., J. O. Peterson et al., 1973; Ellis, 1975). Alternatively, dose is expressed as an Al/P molar ratio by dividing moles of aluminum added by moles of P removed (S. A. Peterson et al., 1974) and dosage to the lake is calculated, based on a knowledge of the P content of the lake volume to be treated. Usually the dose of aluminum chosen is small enough that drastic shifts in pH and residual dissolved aluminum (RDA) do not occur.

The second approach to dose determination allows maximum application of aluminum to bottom sediments and thus emphasizes long-term control of P recycling. Again, laboratory jar tests are employed but dose is determined by changes in pH and RDA, with P removal as a secondary consideration (Kennedy, 1978; Cooke et al., 1978). Initially, dissolved aluminum concentrations are high (Figure 2). As aluminum dose is increased, pH and alkalinity decrease. In the range pH 7 to 5.5, hydroxide floc is formed and dissolved aluminum concentrations are minimal. As pH and alkalinity continue to decrease with increased dose, dissolved aluminum concentrations increases exponentially and then linearly with dose. A dose producing an acceptable pH and RDA concentration is then chosen. Using this method, Kennedy (1978) and later Cooke et al. (1978) defined a "maximum" dose as that dose above which dissolved aluminum concentration exceeds 50 µg Al/l, a concentration Everhart and Freeman (1973) had shown to be safe for rainbow trout. Titration of lake water samples from several depths and thus of varying alkalinity allowed the establishment of a linear relationship between RDA, alkalinity, and dose, which was then employed for lake-scale appliations of alum to Dollar and West Twin Lakes, Ohio. Although a secondary consideration, P removal from the treated water column exceeded 90%.

It should be noted that this approach is not suitable for lakes of low alkalinity because the dose would be too low to exert control of P release. An alternative approach, perhaps first suggested by A. R. Gahler and C. F. Powers of the Pacific Northwest Laboratory of the USEPA and used by Dominie (1978), among others, is to added both alum and sodium aluminate at the same time, calculating how much of each is needed to maintain a pH at which RDA will not increase. Theoretically as much aluminum as desired or as affordable could be added under this procedure.

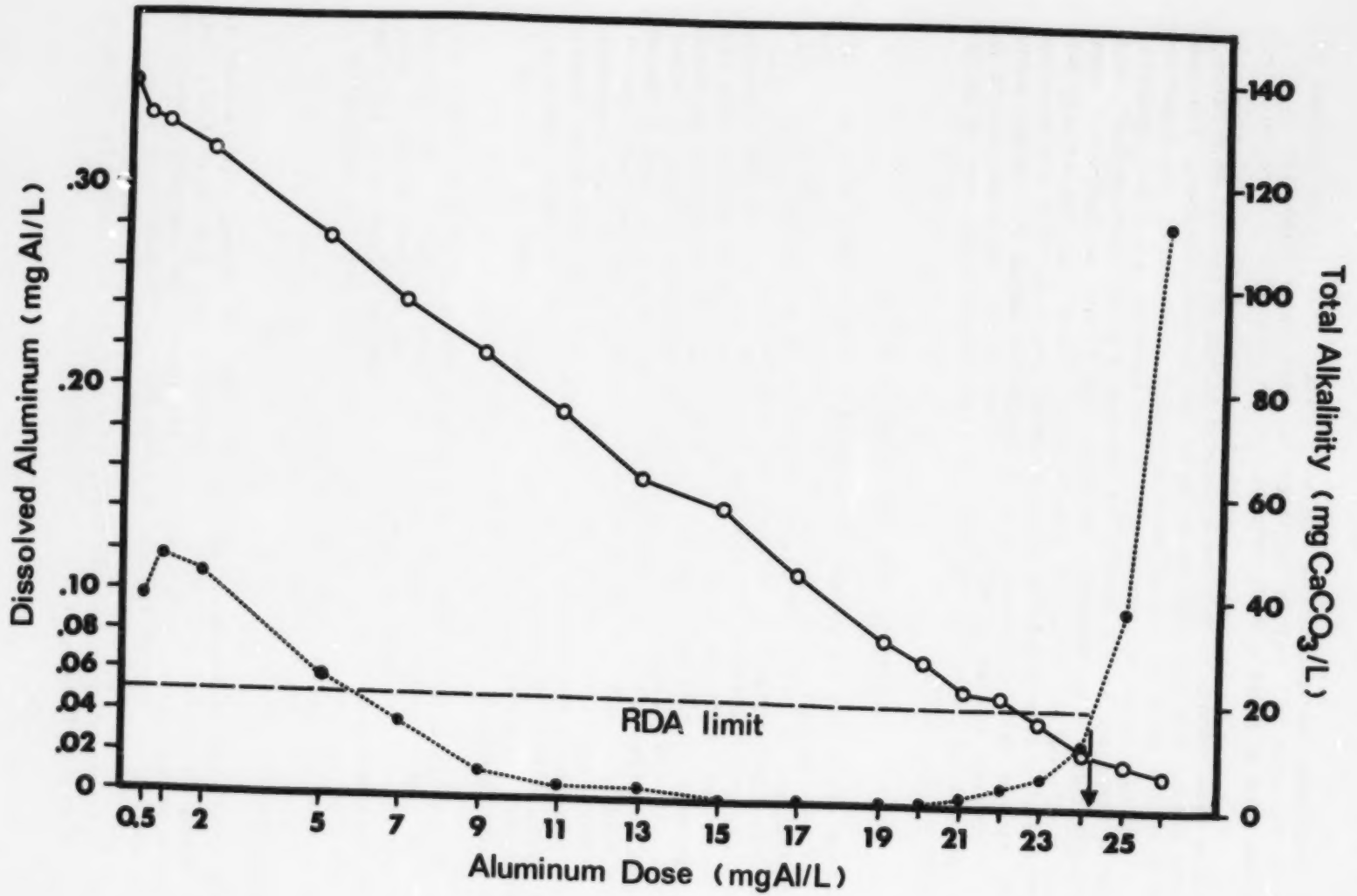


Figure 2. Relationships of aluminum dose, residual dissolved aluminum, and lake water alkalinity (from Cooke et al., 1978).

When aluminate is used alone, pH will rise. This can be avoided by neutralizing it with HCl before addition to soft water (Sanville et al., 1976), as was done at Cline's Pond, Oregon.

The dose requirements to achieve a desired period of control of P release are not now known, and this must be a topic for further research. The main source of P to the water column of many eutrophic lakes during the summer is internal P release (e.g., Larsen et al., 1975; Cooke et al., 1977; Dominie, 1978). While there are biotic sources of internal P (fish, macrophytes), much of it probably comes from anaerobic sediments and P must be controlled there to achieve P limitation of algal populations. Therefore, the Kennedy and Cooke method or the alum-aluminate balance method should be used, and aluminum should be applied well in excess of that needed to remove P from the water column. P removal as the principal objective of the treatment should be reserved for special cases such as the interception of P from decaying macrophytes (Funk et al., 1977).

Suggested Dose Determination Method

Aluminum solubility is minimal between pH 6 to 8, a range also favorable for removal of inorganic and particulate P. Therefore, a dose of aluminum sulfate sufficient to reduce pH to 6.0 is considered an "optimal" dose. RDA, which is independent of dose at this pH, will remain below toxic levels (i.e., < 50 µg Al/l) and the amount of aluminum hydroxide applied to the sediments will be maximized. Outlined below is a simplified method for determining such a dose. Non-metric units are used for the alum since it is supplied in pounds or gallons. Similarly, construction materials are supplied in feet or inches. This method requires minimal laboratory facilities and can be used to determine alum doses for lake treatments in which sediment "sealing" for P control is the primary objective. Prior to initiation of such a lake treatment, decisions concerning the area(s) and/or depth(s) of the lake to be treated must be made. Since this dose drastically reduces pH, potential short-term toxic effects in treated areas should be considered. Many of these can be avoided if treatment is confined to the hypolimnion.

The P precipitation/inactivation technique should be used in lakes with moderate to high retention times (several months or longer). Applications without sufficient diversion of nutrients, such as occurred at Bluff Lake, Illinois (Kothandaraman et al., 1978), will be futile. Lakes with low alkalinity will exhibit excessive pH shifts unless the lake is buffered or a mixture of alum and sodium aluminate are used.

Procedure:

(1) Obtain water samples from several areas and depths. The number of samples needed will vary from lake to lake. For lakes exhibiting wide variation in alkalinity, the number of samples should be sufficient to span the entire range of alkalinities.

(2) Determine the total alkalinity of replicate subsamples by titration with 0.02 N H_2SO_4 to a pH 4.5 endpoint.

(3) Determine the dose of aluminum sulfate required to reduce the pH of replicate samples to pH 6.0. Since granular aluminum sulfate dissolved slowly, stock solutions of liquid or pre-dissolved alum should be used. Additions can be made using a burette or graduated pipette. The concentration of stock solutions should be such that the maximum dose to each one liter lake water sample can be reached by an addition of between 5 to 10 ml. Reaction vessels should be stirred using an overhead stirring motor until pH at final dose (i.e., pH 6.0), determined by continuously monitoring with a pH meter, has stabilized (approximately 2 to 5 minutes). Convert the volume of alum stock solution used to a mass per unit volume dose (i.e, mg Al/l) for each sample.

(4) Determine the linear relationship between dose and alkalinity using the information obtained from the above treatments. This can be accomplished by simple regression analysis or by carefully plotting dose vs. alkalinity. This relationship can then be used to determine the dose at any alkalinity within the range tested. The relationship obtained for a particular lake should not be applied to other lakes.

(5) As described in subsequent paragraphs (see "Application Procedures"), the lake is divided into convenient treatment areas for ease and accuracy of dose. The total amount of alum to be added to each area is a function of the area's volume and the alkalinities of each stratum (usually each meter). Alkalinity of each one meter stratum is measured. Based upon the relation between dose and alkalinity, the maximum dose for each depth interval is calculated from the maximum dose in mg Al/l to alum/m^3, using a formula weight of 594.19 ($Al_2(SO_4)_3 \cdot 14\ H_2O$) and a conversion factor of 0.02428 to change mg Al/l to pounds (dry) alum/m^3.

(6) If liquid alum is to be used, further calculations are necessary to express the dose in gallons of alum/m^3. Details are given in Cooke et al. (1978). Briefly, commercial alum ranges from 8.0 to 8.5% Al_2O_3, equivalent to 5.16 to 5.57 pounds dry alum per gallon at 60°F. Alum is shipped at temperatures near 100°F and will thus have lower density. The percent Al_2O_3 (at 60°F) is supplied by the shipper and this is converted to density, expressed as degree Baume' using Figure 3. A temperature correction is applied against this Baume' number, using Figure 4, to account for the decrease in density. The supplier can estimate the temperature, or it can be checked at the delivery site. Adjusted Baume' is obtained by subtracting the correction factor from the 60°F Baume'. Pounds of alum at shipping temperature are obtained using the adjusted Baume' and Figure 5.

(7) Maximum dose at each depth interval, calculated earlier as pounds of alum (dry)/m^3, is converted to gallons/m^3 by dividing by the value, in pounds per gallon, obtained from Figure 5. Total dose is finally

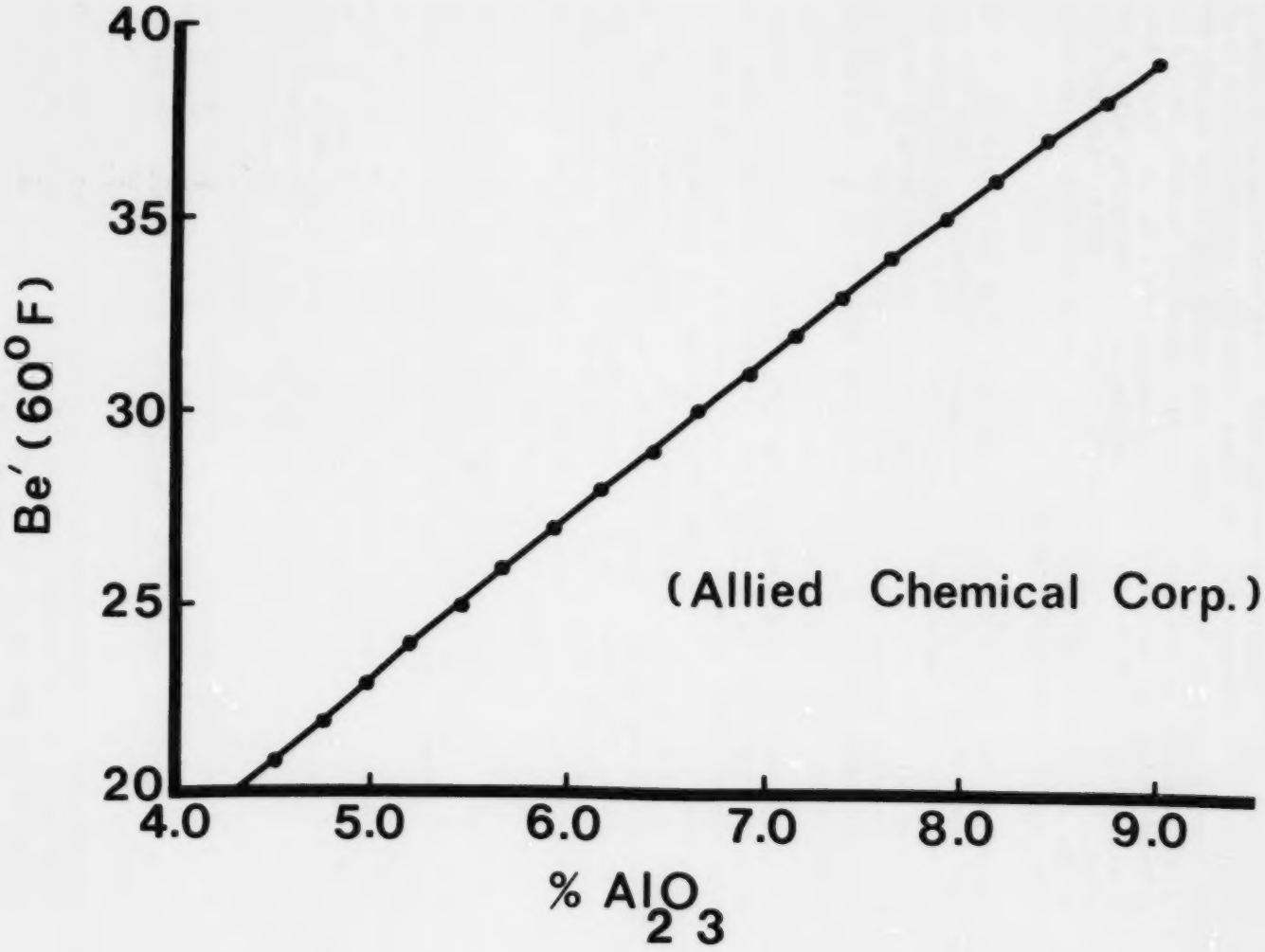


Figure 3. Relationship of Baume' (60°F) and percent Al_2O_3 (from Cooke et al., 1978 as adapted from Allied Chemical Corp. Technical Bulletin).

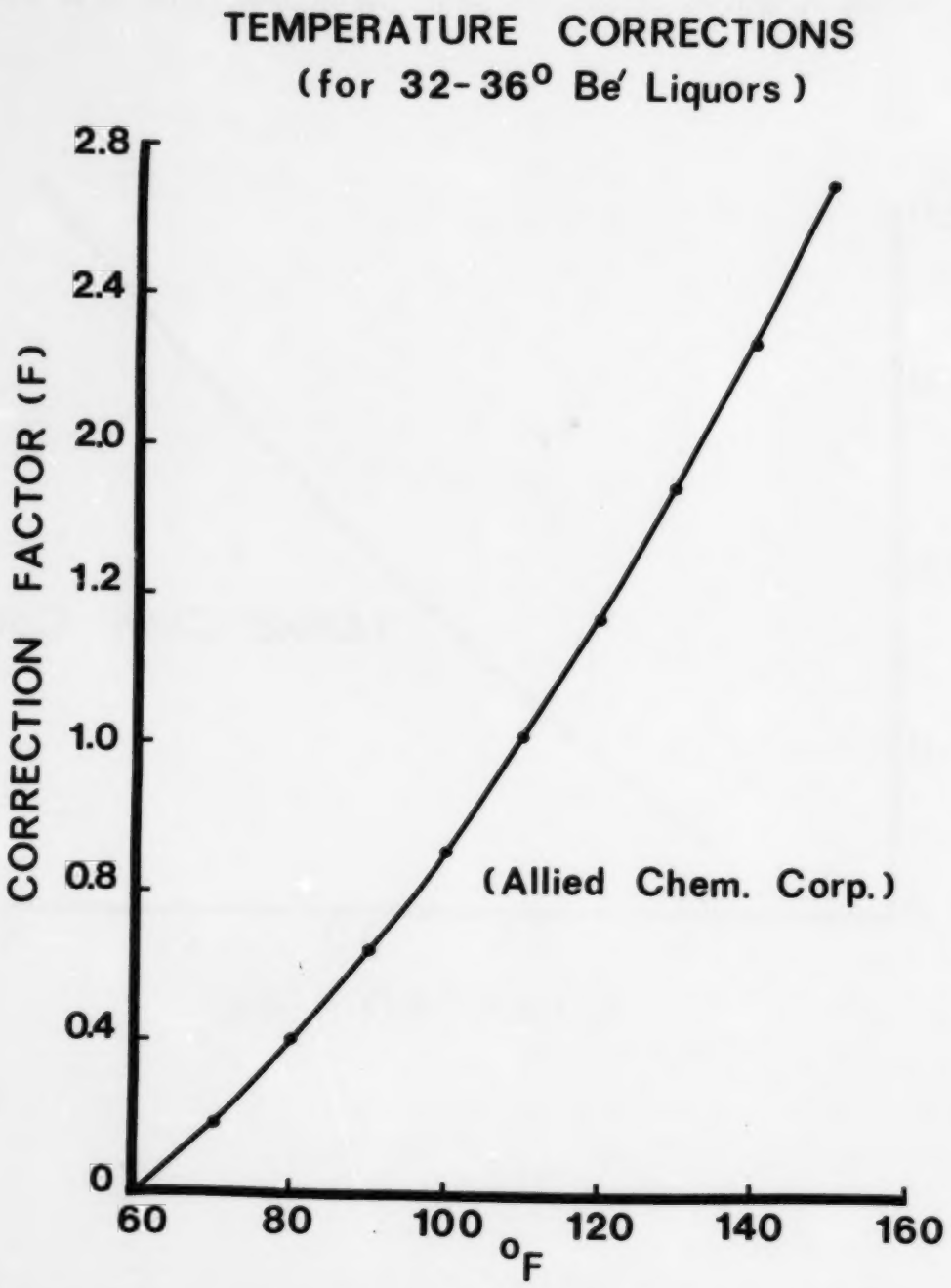


Figure 4. Temperature correction factors for 32-36° Be' liquors (from Cooke et al., 1978 as adapted from Allied Chemical Corp. Technical Bulletin).

obtained for a treatment area by knowing the volume of each stratum, multiplying the volume by the maximum dose in gallons/m^3, and summing. The sum is applied to the area (e.g., top of hypolimnion to be treated.

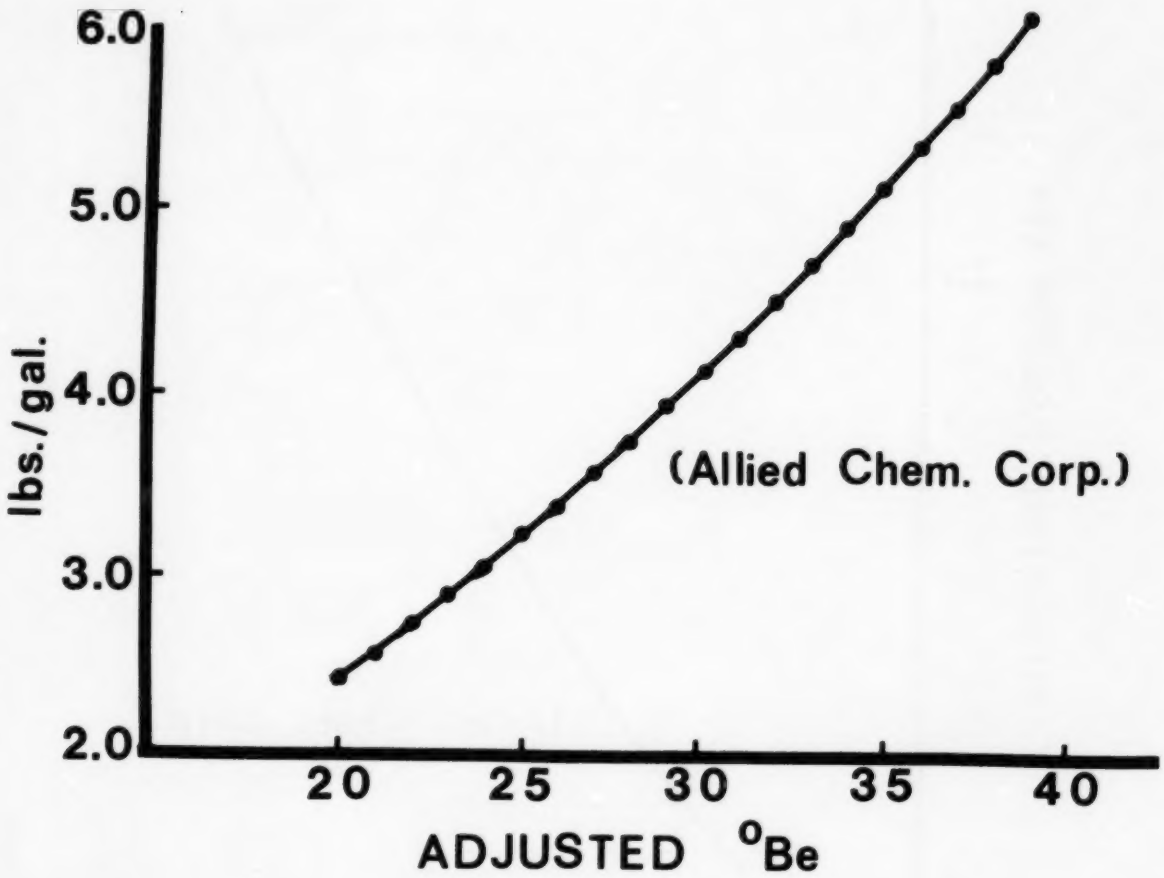


Figure 5. Curve to determine pounds of alum/gallon based on adjusted Baume' (from Cooke et al., 1978 as adapted from Allied Chemical Corp. Technical Bulletin).

2. Chemical Form

Nearly all treatments since Lake Langsjon (Jernelov, 1970) in 1968 have been with liquid alum or sodium aluminate, applied with extensive mixing to surface or hypolimnetic waters (Table 1). Dry alum does not form a floc as

Table 1. Summary of Phosphorus Inactivation/Precipitation Treatments

Lake	Chemical-Physical Data	Date	Chemical and Dose	Objective and Site of Application	Duration of Effectiveness	Cost	Side-Effects
1. Dorrdrecht Reservoir Netherlands Peelen (1969)	No Data*	1962	2 g Fe^{+3}/m^3	P removal. Surface	No Data	No Data	No Data
2. Langsjon Lake Stockholm, Sweden Jernelov (1970)	A_o = 35 ha V^o= 6.5 x 10^6 m^3 z = 3.0 m max	4/68	4.7 g Al/m^3 Granular alum	P removal. Surface	Unknown	No Data	None Reported
3. Lötsjön Lake Stockholm, Sweden Hellstrom (1979)	A_o = 6 ha V^o= 1.2 x 10^5 m^3 $\bar{z}$ = 3.0 m max z = 2.0 m pH = 8.0 polymictic	1968 1969 1970 1974 1975	3.2-7.7 g Al/m^3 Granular alum	P removal. Surface	1-6 months	No Data	None Reported
4. Horseshoe Lake Manitowac Co., Wisconsin J. O. Peterson et al. (1973)	A_o = 8.9 ha V^o= 3.6 10 10^5 m^3 $\bar{z}$ = 16.7 m max x = 4.0 m Alk = 218-278 mg/l pH = 6.8-8.9 dimictic	5/70	2.6 g Al/m^3 Liquid alum	P removal. Surface	2-3 years	$101/ha for alum 12 man-days for applic. 1.33 man-days/ha	None Observed
5. Cline's Pond Corvallis, Oregon Sanville et al. (1976)	A_o = 0.4 ha V^o= 9600 m^3 $\bar{z}$ = 4.9 m max z = 2.4 Alk = 30-50 mg/l pH 7.0-7.7 monomictic	4/71	10 g Al/m^3 Liquid sodium aluminate and HCl	P removal and control of P release. Surface	1 year	$420/ha	None Reported
6. Fishery Ponds Waterville, Minn. Bandow (1974)	A_o = 0.4 ha V^o= 0.6 x 10^5 m^3 $\bar{z}$ = 2.1 m max z = 1.5 m Alk = 150 mg/l pH = 8.0	5/71 6/72 6/73	8.4 g Al/m^3 4.2 g Al/m^3 5.6 g Al/m^3 Liquid alum	P removal. Surface	Unknown	No Data	None observed to fish and zooplankton
7. Söndra Hörken Grangesburg, Sweden Ahling and Raghall (1973) Dunst et al. (1974)	A_o = 15 ha z^o= 22 m max	1971	160 tons Granular alum	P removal. Surface	2 years	No Data	None Reported
8. Braidwood Lagoon Braidwood, N.S.W. May (1974)	z = 0.9 m max pH = 6.3	7/71	10.7 g Al/m^3 Liquid alum 31 g Fe^{+3}/m^3 Dry ferric alum	P removal and control of P release. Alum to surface, iron to pond bottom	Unknown	No Data	None Reported

(continued)

Table 1. (continued)

Lake	Chemical-Physical Data	Date	Chemical and Dose	Objective and Site of Application	Duration of Effectiveness	Cost	Side-Effects
9. Snake Lake Villas—Oneida Cos. Wisc. T. Wirth and R. P. Narf (unpub.)	A_o = 5.0 ha z^o= 5.5 m max Alk = 50 mg/l dimictic	5/72	9.0 g Al/m^3 Liquid alum and sodium aluminate; surface dilutional pumping	P removal and control of P release. Surface	To Present	No Data	None observed to macro-invertebrates
10. Long Lake, Langlade Co. Wisc. T. Wirth and R. P. Narf (unpub.)	A_o = 28 ha z^o= max Alk = 7 mg/l	5/72	14 gal/m^3 Liquid alum and sodium aluminate at surface	P removal and effect on pH and alkalinity	Unknown	No Data	None observed to macro-invertebrates
11. Reither See Tyrol, Australia Dunst et al. (1974) Findenegg (1972)	A_o = 1.5 ha z^o= 8.2 m max	5/72	6 g Fe^{+3}/m^3 $FeCl_3$ and hypolimnetic siphoning	P removal. Surface	Unknown	$120/ha	Unknown
12. Powderhorn, Minneapolis, Minn. Dunst et al. (1974)	A_o = 3.2 ha z^o= 7.0 max	8/72	Unknown dose Liquid alum	P removal. Surface	Unknown	$563/ha	Unknown
13. Mytajärvi Lahti, Finland Dunst et al. (1974)	A_o = 1.5 ha z^o= 10.5 m max	4/73	24 g Al/m^3 Granular alum	Unknown objective. Surface (ice)	Unknown	No Data	Unknown
14. Pickerel Lake, Portage Co., Wisconsin T. Wirth and R. P. Narf (unpub.)	A_o = 20 ha $\bar{z}^o$= 4.6 m max $\bar{z}$ = 3.0 polymictic pH = 8.2 Alk = 110 mg/l	4/73	7.3 g Al/m^3 Liquid alum	P removal. Surface	Unknown	No Data	None observed on benthic macroinverte-brates
15. Welland Canal Welland, Ontario Shannon et al. (1974)	A_o = 74 ha V^o= 6.2 10^6 m^3 $\bar{z}$ = 9 0 m max $\bar{z}$ = 9.0 m Alk = 109 mg/l dimictic	5/73	2.5 g Al/m^3 Liquid alum surface	P removal	1 year (end of monitoring)	$204/ha for all equip. and chemicals $161/ha for chemicals 100 man-days for chem. applic.: 1.35 man-days/ha	None observed to zoo-plankton
16. Cline's Pond Corvallis, Oregon Powers et al. (1975)	A_o = 0.4 ha V^o= 9600 m $\bar{z}$ = 4.9 m max $\bar{z}$ = 2.4 m Alk = 30 mg/l pH = 7.0-7.7 monomictic	3/74	5 g Zr/m^3 and NaOH $ZrCl_4$	P removal. Surface	Unknown	No Data	None Observed

(continued)

Table 1. (continued)

Lake	Chemical-Physical Data	Date	Chemical and Dose	Objective and Site of Application	Duration of Effectiveness	Cost	Side-Effects
17. Lyngby Sø Sweden Sønnichsen (1978)	A_o = 59 ha $\bar{V}^o$= 1 x 10^6 m^3 $\bar{z}$ = 1.69 m pH = 9.0	5/74	2 Doses, 8.6 and 20.2 g Al/m^3 Granular alum	P removal. Surface	Transitory	No Data	Flocculation and possible toxicity to micro-crustacea
18. Calusa Lakes (2) Miami, Florida Haumann and Waite (1978)	A_o = 1.38 ha z^o= 4.3 m max Alk = 46-188 mg/l pH = 7.0-9.2	6/74	1.2 g Al/m^3 Liquid alum	P removal to control macrophytes. Surface	Unknown	No Data	None Reported
19. Morse's Pond Wellesly, Mass. Thompson (unpub. mss.)	A_o = 44.5 ha V^o= 113.6 x 10^5 m^3 $\bar{z}$ = 5.5 m max z = 2.6 unstratified	7/74	3.3 g Al/m^3 Liquid alum plus aeration and copper	P removal. Surface	Unknown	No Data	None Reported
20. Dollar Lake Kent, Ohio Kennedy (1978)	A_o = 2.2 ha V^o= 0.86 x 10^5 $\bar{z}$ = 7.5 m max z = 3.9 m pH = 6.7-8.6 Alk = 101-127 mg/l dimictic	7/74	20.9 g Al/m^3 Liquid alum	P removal and control of P release. Surface (10% of dose) and hypolimnion	To Present	$504/ha for chemicals 4.3 man-days/ha	None Observed
21. Liberty Lake Spokane, Washington Funk and Gibbons (1977)	A_o = 288 ha $\bar{V}^o$= 20.2 x 10^6 m^3 z = 7.0 m pH = 6.6-9.3 Alk = 12-65 mg/l dimictic	10/74	0.52 g Al/m^3 Liquid alum rotenone	P removal and interception of P release from delaying macrophytes. Surface	2 years	No Data	None Observed
22. West Twin Lake Kent, Ohio Cooke et al. (1978)	A_o = 34 ha V^o= 14.2 x 10^4 m^3 $\bar{z}$ = 11.5 m max z = 4.4 m Alk = 102-149 mg/l dimictic 16 ha treated	7/75	26 g Al/m^3 Liquid alum	Control of P release. Hypolimnion	To Present	$425/ha for chemicals and equip. 0.94 man-days/ha	Decrease in micro-crustacea diversity
23. Lake San Marcos Orville Ball, Assoc., Consultants (unpub. mss.)	A_o = 18.2 ha V^o= 4.3 x 10^5 m^3 $\bar{z}$ = 2.3 m max z = 2.3 m pH = 7.3-9.1 Alk = 190-268 mg/l	7/75	6 g Al/m^3 Liquid alum	P removal. Surface	Unknown	$126/ha	None Reported

(continued)

Table 1. (continued)

Lake	Chemical-Physical Data	Date	Chemical and Dose	Objective and Site of Application	Duration of Effectiveness	Cost	Side-Effects
24. Bluff Lake Fox Chain, Illinois Kothandaraman et al.	A_o = 37.2 ha V^o= 1.2 x 10^6 m^3 $\bar{z}$ = 8.2 m max z = 3.2 m Alk = 162 mg/l pH = 8.7 dimictic	8/77	8 g Al/m^3 Liquid alum	P removal and control of P release. Surface	Days	No Data	None Reported
25. Medical Lake Medical Lake, Washington Gasperino and Soltero (1978)	A_o = 64 ha V^o= 6.4 x 10^6 m^3 $\bar{z}$ = 18 m max z = 10 m Alk = 750 mg/l pH = 8.5-9.5	8-9/77	12.2 g Al/m^3 Liquid alum	P removal and control of P release. Multiple applications to surface and hypolimnion	To Present	No Data	None Reported
26. Mirror Lake Waupaca, Wisconsin Knauer (1978) (unpub. mss.)	A_o = 5.1 ha V^o= 4 x 10^5 m^3 $\bar{z}$ = 13.1 m max z = 7.8 m Alk = 222 mg/l pH = 7.6 monomictic	5/78	6.6 g Al/m^3 Liquid alum and aeration	P removal and control of P release. Hypolimnion	To Present	1.4 man-days/ha	None Reported
27. Shadow Lake Waupaca, Wisconsin Knauer (1978) (unpub. mss.)	A_o = 17.1 ha V^o= 9.1 x 10^5 ha $\bar{x}$ = 12.4 m max z = 5.3 m Alk = 188 mg/l pH = 7.4 dimictic	5/78	5.7 g Al/m^3 Liquid alum	P removal and control of P release. Hypolimnion	To Present	0.61 man-days/ha	None Reported
28. Annabessacook Lake Winthrop, Maine Dominie (1978 (unpub. mss.)	A_o = 575 ha V^o= 31.1 x 10^6 m^3 $\bar{z}$ = 12 m max z = 5.4 m Alk = 20 mg/l pH = 6.7 dimictic 121.4 ha treated	8/78	25 g Al/m^3 7-10 m contour	Control of P release Hypolimnion	To Present	No Data	None Reported

well and is less effective. In instances where dry alum is the only form available, it can be mixed in tanks to form a slurry before application (e.g., J. O. Peterson et al., 1973).

3. Depth of Application

Depth of application is directly related to the treatment objective. A surface treatment is required for P removal, whereas control of P release from sediments usually involves a hypolimnetic application. Most of the pre-1974 projects were surface treatments, but since then hypolimnetic application has been favored (Table 1) and is recommended since control of P release is the primary objective in most situations and because application to this zone will avoid an inadvertent increase in aluminum or pH in productive areas of the lake. It should be noted however that surface applications are far less costly than hypolimnetic, and could be as effective in controlling P release if sufficient chemical is added.

4. Application Procedures

The methods for application of aluminum salts to lake waters have been remarkably similar over the twelve years in which this technique has been employed in the United States. The basic application system was reported by J. O. Peterson et al. (1973) for Horseshoe Lake, Wisconsin, the site of the first treatment in the United States. Dry alum was mixed on board the vessels by pumping lake water into a slurry tank. A second pump moved the slurry to a manifold pipe (3 m long, performed with 8 mm holes at 30 cm intervals), which was suspended behind the craft just below the surface and perpendicular to the path of travel. Nearly all subsequent applications have used this basic design, although liquid alum has been used in most cases thus avoiding the need for the first pump and mixing tank, but requiring an on board holding tank.

Figure 6 is an illustration of the basic equipment design for the application of liquid alum, modeled after the system used at Dollar and West Twin Lakes, Ohio in 1974 and 1975 (Kennedy, 1978; Cooke et al., 1978). The system consisted of three components: a storage facility, delivery to the barges, and the barges.

Alum was delivered by tank truck to an onshore above-ground swimming pool with a capacity of 28.7 m^3 (7,600 gallons), or about two truck loads. The pool was 10-15 m above lake level, giving gravity assisted pumping out to the loading platform. At poolside, a 12 hp, 2½ inch pump delivered alum through a hose from the pool to a floating platform in the lake. The piping system was a series of 20 foot 2 3/8 inch I.D. PVC rigid wall pipes, floated under anchored 55 gallon drums spaced 10 m apart. The pipe terminated at a butterfly valve. A 6.1 m section of flexible hose, connected to the outflow side of the valve, was used to fill barge tank. Communication from this loading platform to the pump operator at the pool was 2-way radio.

The application barges were designed by Robert H. Kennedy, and consisted of a series of five 55 gallon drums welded end to end. The buoyancy of one drum, subtracting its own weight, is about 400 lbs. These barges had a

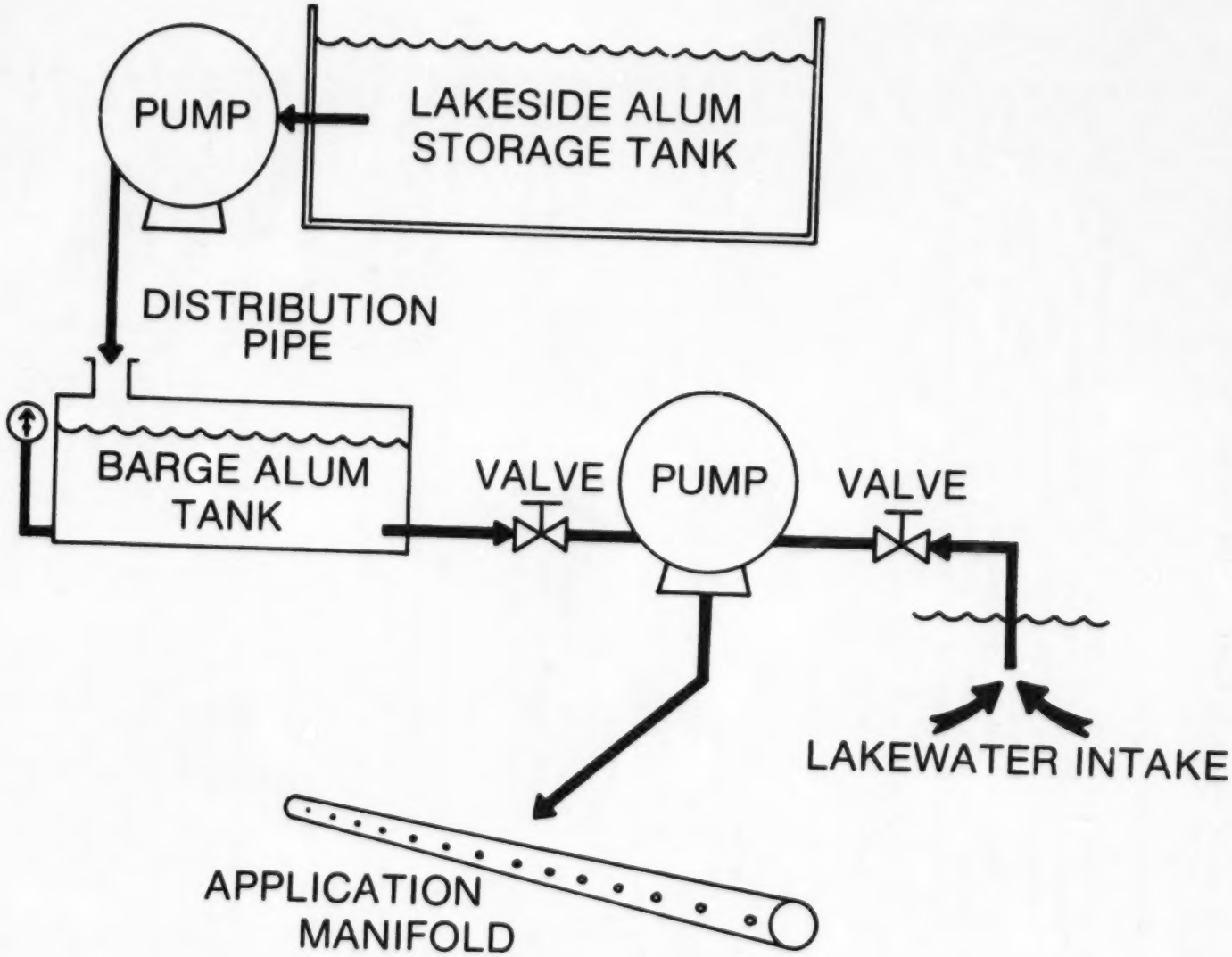


Figure 6. Basic design of aluminum sulfate application equipment.

buoyancy of 10,000 or 12,000 lbs (4,500 to 5,400 kg). The rows of barrels were lashed with 3/8 inch cable to a steel frame made from 4 inch channel iron. A seven meter long application manifold made of 2 3/8 inch I.D. PVC pipe, was suspended below the barge at the depth of application by attaching it to two steel A-frames, which were bolted fore and aft on either side of the barge. (The barges were powered by a 35 hp outboard motor with a work prop.) For travel in shallow water, the A-frames and manifold could be raised to the surface behind the barge. The manifold pipe was capped at the ends and drilled with 1/4 inch holes, oriented bottom and back.

Alum was pumped with a 1½ hp pump to the manifold from two 250 gallon tanks, coupled by their bottom drains with 2¼ inch galvanized pipe. The pump was located on the barge deck and fitted with a tee coupling at the intake, allowing alum from the tanks and lake water to be drawn simultaneously. Damage to pump fitting was slight when they are periodically flushed with fresh water. Flow from each source was maintained by valves at 50/50 to provide initial mixing. Mixing was provided by turbulence from the manifold. The quantity of alum in the tanks was monitored by a graduated plastic standpipe.

In most surface alum applications, the manifold has trailed behind the barge and the only mixing has been that provided by the manifold itself. Funk et al. (1977) used a frontal distribution system to take advantage of the mixing and spreading action of the barge's pontoons and the fast mixing action of the propellers of the motor. This modification may provide far more effective sorptive action of the aluminum hydroxide.

Special application designs have been employed for the simultaneous addition of sodium aluminate and aluminum sulfate to soft water lakes, and for the addition of ferric alum and dry aluminum sulfate to small ponds. Dominie (1978) describes the use of a 6,000 gallon (22.7 m^3) three-compartmented tank truck, mounted on a 40 x 25 ft (1,000 ft^2; 9,219 m^2) barge. Each compartment delivered material via pumps to a completely segregated dual diffuser or manifold, made of 2 inch blank iron pipe which hung below the barge at the 8 m level (hypolimnetic treatment of Annabessacook Lake, Maine). Sodium aluminate and aluminum, sulfate had to be pumped separately since contact prior to release to the water would clog equipment with the precipitate formed. May (1974) added aluminum sulfate to ponds by mixing dry alum in drums and then returning the mixture to the pond. Ferric alum was then added by placing blocks of it in the water, suspended by floats, and allowing it to dissolve. Blocks were replaced over the year as they dissolved.

Most of the equipment described above was designed to give even dose and surface coverage, or to add alum to the hypolimnion. These application methods can be tedious and expensive, particularly when the cost of building equipment is considered (see later section on cost estimates). An alternative procedure would be to spray the alum on the lake surface with large diameter hoses and a large velocity pump. This would result in considerable savings in manpower and equipment costs. Several serious problems could arise, including localized lethality due to high aluminum or hydrogen ion concentrations from uneven distribution of chemical, and poor mixing also leading to locally very

heavy amounts of floc. On small lakes or ponds this method of application could be effective, particularly if boats could be used to create turbulence and mixing.

An even coverage of lake surface or hypolimnetic area has usually been accomplished with a grid design. This procedure is well illustrated by the work of Funk et al. (1977), who divided Liberty Lake, Washington in four areas, which were then divided into subsections and marked by buoys (Figure 7). Each section could be identified by the barge operator from the color of the buoys, and from an accompanying enlarged sectional map carried on board. The map was also marked with the number of bags of alum required for each section. This application plan has been the basic type since it was first used at Horseshoe Lake (J. O. Peterson et al., 1973). For hypolimnetic treatments, the area to be treated is marked at the lake surface, but each subsection within that area receives a different amount of liquid alum (assuming a maximum dose as earlier defined is to be applied), depending upon the subsection's volume and total alkalinity. These data are marked on the onboard map so that barge operators can apply a full dose (Cooke et al., 1978).

5. Optimum Time for Application

The optimum time for application has been debated. If P removal is the objective then early spring is ideal since, as pointed out by Browman et al. (1977) and Eisenreich et al. (1977), most of the P in the water column at this time is inorganic P, a form almost completely removed by the floc. In the summer months a large fraction of total P is in the particulate and dissolved organic fractions, and dissolved organic P is efficiently removed with aluminum. If control of P release is the objective of the treatment then time of application appears not to be as critical since it is the sediments which are the target and not P in the water column. Since barges are slow and unmaneuverable, and may sail on windy days, application should be on calm days.

6. Toxicity of Aluminum

The toxicity of aluminum to aquatic biota has been reviewed by Burrows (1977). The relatively sparse data on freshwater organisms allow no generalizations about toxicity to taxonomic or habitat-related groups. Freeman and Everhart (1971) and Everhart and Freeman (1973) carried out one of the most thorough studies of aluminum toxicity and pointed out that few investigators have accounted for the complex chemistry of aluminum in water. This was noted as well by Borruws (1977). The amount of residual dissolved aluminum (RDA) is pH dependent and some test waters could receive large amounts of aluminum before RDA became sufficiently high to be toxic. Thus reports of safe dose limits, unless actual RDA is measured in the test and alkalinity-pH reported, are of limited value since they report aluminum added, not dissolved aluminum in the water. There is very little direct laboratory or field evidence about the short or long-term effects of aluminum on aquatic biota or aquatic communities.

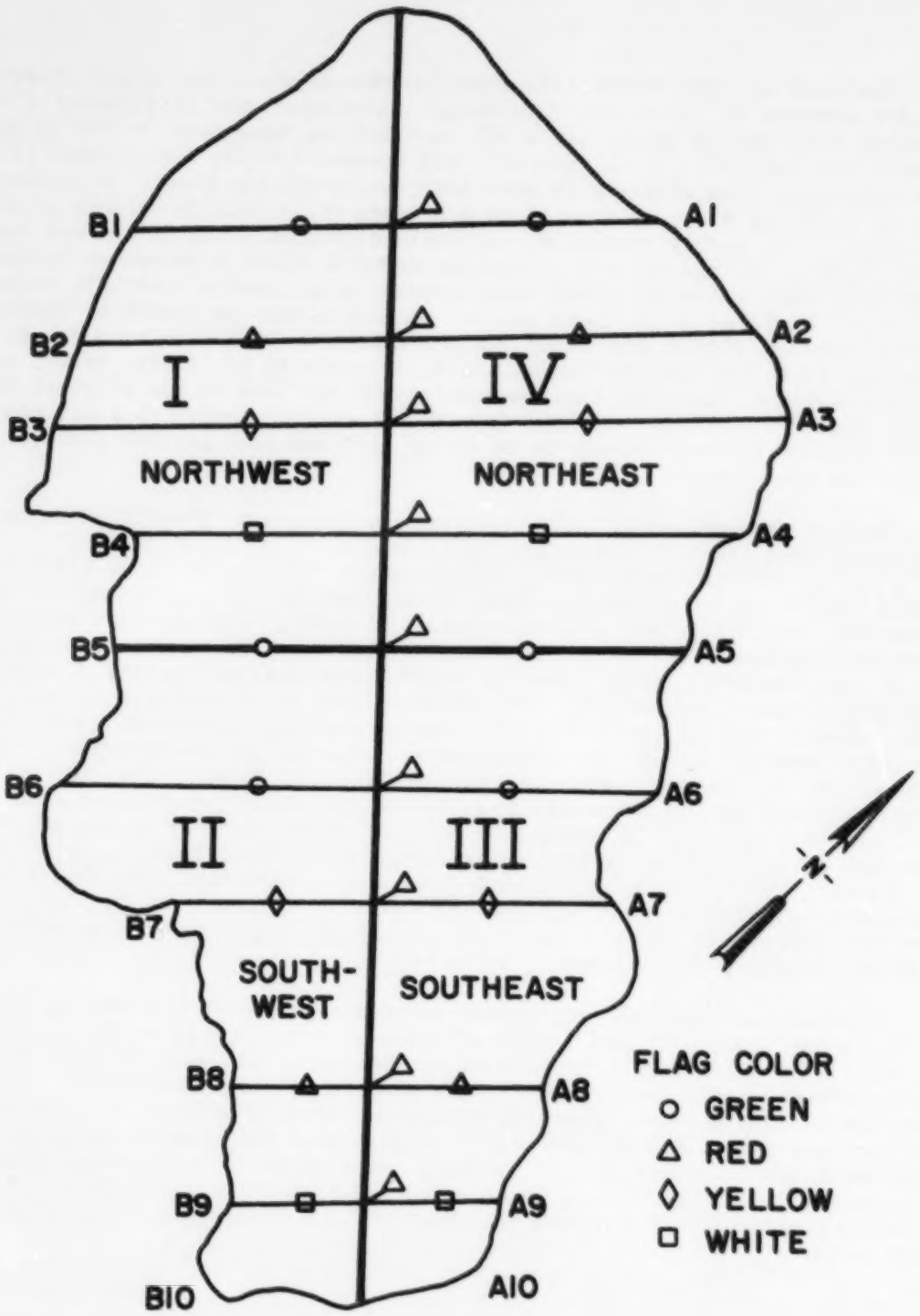


Figure 7. Division and delineation of treatment sections for aluminum sulfate treatment of Liberty Lake, Washington (from Funk and Gibbons, 1978).

There are at least three laboratory studies in which the actual chemistry of this element in water was considered. Biesinger and Christensen (1972) reported that Daphnia magna had a 16% reproductive impairment at 320 µg Al/l. Freeman and Everhart (1971), Everhart and Freeman (1973), and Freeman (1973) used a constant flow bioassay to test toxicity to rainbow trout. A concentration of 5,200 µg Al/l, whether at pH 9.0 where it is totally soluble or at pH 7.0 where it is nearly insoluble, seriously disturbed trout if present longer than 6 weeks. At 520 µg Al/l, symptoms appeared after a few weeks exposure, suggesting that the usual short-term bioassay might have missed this response entirely. At 52 µg Al/l, there was no obvious effect on growth or behavior, leading Kennedy (1978) and Cooke et al. (1978) to adopt this value as the upper RDA limit for lake treatment. S. A. Peterson et al. (1974, 1976), using static bioassays, reported that Chinook salmon survived an RDA of about 20 µg Al/l. Higher concentrations were not tested. Daphnia magna did not reach a 96 hr TL_m with concentrations up to 80 µg Al/l RDA, but percent survival was reduced to about 60%.

Several investigators have reported an apparent absence of negative effects on fish (Kennedy and Cooke, 1974; Bandow, 1974; Sanville et al., 1976) or benthic invertebrates (Narf, 1978) after full-scale lake treatments. Narf's report is of particular importance since it represents monitoring of Horseshoe, Long, Pickerel, and Snake lakes, Wisconsin, the earliest full-scale aluminum treatments in the United States (Table 1). Cooke and Myers (unpub. mss.), and Moffett (1979) found a significant decline in the Shannon H' diversity (Shannon and Weaver, 1959) of planktonic microcrustacea in West Twin Lake, Ohio, after a hypolimnetic aluminum sulfate treatment, when post-treatment samples (1976 and 1978) were compared to pre-treatment (1969) samples or to the untreated downstream lake. The diversity decline was apparently not due to aluminum toxicity in the water column (see also West Twin case history) but to changes in type of algae cells or to low pH and/or high RDA in interstitial waters where ephippia, or other resting stages might be found. Their results could not have been predicted from the standard laboratory bioassay, pointing out that future toxicity studies should be directed toward the actual level of biological organization to which the aluminum treatment is directed.

Aluminum toxicity does not appear to be a significant problem, as long as pH is controlled and/or RDA is not allowed to reach levels in the area of 50 µg Al/l. The long-term effects seem to be small, at least to most benthic invertebrates which live directly in the aluminum-enriched sediments. Effects upon the community level organization are essentially unknown but the report of Cooke and Myers, and Moffett (1979) suggest that the response of this level must be further investigated. In areas where lakes have low alkalinity and acid rainfall is significant, lowering of lake pH could occur years after an aluminum treatment with a sudden increase in RDA and possible toxic effects to lake biota.

IV. Case Histories of Phosphorus Precipitation-Inactivation

A. Introduction

There have been at least 28 reported uses of the phosphorus inactivation/precipitation technique, all of them since 1962, and nearly all with aluminum. Many of these projects have little or no documentation of long-term effects. All are listed in Table 1, along with available data on lake characteristics, dose, method of application, cost and side-effects. The reader is urged to consult reports or one or more of the persons listed for detailed guidance for a particular lake type or problem.

Seven different treatments have been selected for more detailed review because they are representative of a particular approach, or have a long period of monitoring of the effects, or because they seem to best illustrate the strengths and shortcomings of the technique. In general there have been few treatments for which published documentation is available and even fewer for which sufficient post-treatment monitoring has occurred.

B. Case Histories

1. Horseshoe Lake, Wisconsin

The first reported phosphorus precipitation in the United States was at Horseshoe Lake, Wisconsin (J. O. Peterson et al., 1973). Their results are important because they describe the mechanics of a surface application, have been monitored for effects longer than any other study, and because this project illustrates the need for adequate diversion of nutrient income and application of sufficient aluminum to control P release from the sediment.

Pertinent limnological data are listed in Table 2. The lake had experienced algal blooms, dissolved oxygen depletions and fish kills prior to treatment. The authors attribute the high nutrient levels to agricultural and natural drainage, and to a cheese-butter factory which discharged wastes to the lake before closing in 1965.

Table 2. Physical-Chemical Data for Horseshoe Lake (from J. O. Peterson et al., 1973)

Location:	Manitowac County, Wisconsin
Watershed Area:	700 ha
Lake Area:	8.9 ha
Maximum Depth:	16.7 m
Mean Depth:	4.0 m
Volume:	3.6×10^5 m^3
Water Residence Line:	0.7 yrs
Thermal History:	dimictic
pH Range:	6.8-8.9
Total Alkalinity Range:	218-278 mg/l as $CaCO_3$

The goals of the Horseshoe Lake project were to demonstrate that alum could be applied safety and effectively to a lake, to document the effects of the alum on water chemistry and algae, and to determine the costs. It was expected, based upon the Swedish experience (Jernelov, 1970), that there would be at least a short-term decreased in total P and improved oxygen conditions.

The object of the treatment was to remove P from the water column. The dose was determined by jar tests and it was found that 71% removal of total P could be achieved with a dose of 225 g $Al_2(SO_4)_3 \cdot 14\ H_2O/m^3$ (16.7 g Al/m^3). While a dose of 18 g Al/m^3 was proposed, 10.2 metric tons were actually applied to the lake surface (2.1 g Al/m^3), as liquid alum.

Three applicator vessels of different sizes were used to distribute the alum, and these are described in detail in their report.

The lake was divided into 9 plots, each 1 hectare, and a predetermined amount of alum was added to each, just below water surface, on 20 May 1970. The P content in 1971 and 1972 was much lower than 1966, and significant decreases were observed in both the epilimnion and hypolimnion. While the normal summer increase in P did not occur in 1970, there was no decrease below pre-treatment levels until after fall circulation, at which time there was a substantial decrease. A similar observation has been made since then in the cases of the hypolimnetic treatments at Medical Lake and Annabessacook Lake (Gasperino, 1978; Dominie, 1978, respectively).

Hypolimnetic P in Horseshoe Lake has increased slightly every year since treatment (up to 1978) although it has never reached the levels found before the applications (Born, 1979). Their treatment gave about 8 years of control of hypolimnetic P concentration.

Secchi disc transparency increased, few algal blooms occurred in 1970, and there were no fish kills through 1972. Lake shore residents were reported to be pleased. No data have been reported about algae since 1970. Nitrogen fractions were higher than anticipated after treatment, and dissolved oxygen conditions were greatly improved. Surveys through 1978 have indicated no detrimental side effects to benthic insect larvae.

2. Dollar Lake-West Twin Lake, Ohio

The alum treatment of Dollar Lake in July 1974 and West Twin in July, 1975 differed from earlier applications in these respects: 1) application was hypolimnetic; 2) the objective was control of P release from anaerobic sediments; 3) dose was not based on P removal in jar tests but upon the maximum amount the hypolimnion could receive before a pre-defined level of RDA was approached; and 4) the West Twin treatment was compared to changes in a similar, adjacent and untreated lake.

The Twin Lakes and Dollar Lake are located in a small residential watershed in northeastern Ohio. Pertinent features of the watershed and lakes are listed in Table 3 and thorough descriptions are given in Kennedy (1978) and Cooke et al. (1978).

Table 3. Physical-Chemical Data for Dollar-Twin Lakes

Location:	West Twin	East Twin	Dollar
Watershed Area:	---	Portage Co, Ohio	---
Watershed Area:	---	355 ha	---
Lake Area:	34.02	26.88	2.22
Maximum Depth (m):	11.50	12.00	7.50
Mean Depth (m):	4.34	5.03	3.89
Volume (m^3):	14.99 10^5	13.50 10^5	1.86 10^5
Water Residence Time:	1.28	0.58	----
Thermal History:	---	all are dimictic	---
pH Range:	6.9-8.5	6.9-8.3	6.7-8.6
Alkalinity Range (mg/l as as $CaCO_3$):			
Data From: Cooke et al. (1978), Kennedy (1978)			
Application Area (ha):	16	--	1.39

The lakes became very eutrophic in the late 1960s due to septic tank drainage and urban runoff, and had a Carlson (1977) Tropic State Index about 65 (hyper-eutrophic). In 1971-72, septic effluent was diverted but recovery was slow, due in part to internal release of P (Cooke et al., 1977), and the lakes continued to exhibit blooms of blue-green algae and extensive macrophyte areas.

Kennedy and Cooke (1974) suggested that alum dose could be based upon alkalinity and the criterion that alum could be added to lake waters until there is sufficient pH change to bring about a residual dissolved aluminum concentration of 50 µg Al/l, a level shown to be safe for trout (Everhart and Freeman, 1971). A step-by-step evaluation of this concept followed, including a test of long term effectiveness in enclosures in the lake (Kennedy, 1978), and toxicity tests to the Northern Fathead Minnow (Wilbur, 1974). A pilot application to Dollar Lake followed this work.

Dollar Lake received 10.2 tons of alum (2,896 gallons or 11 m^3), 10% of which was added to the surface, on 19 July 1974. Details of dose calculation and application are given in Kennedy (1978), and described in Section III of this report. Application of aluminum sulfate to West Twin was made to the 5 meter contour, an area of 16.04 ha. A total of 36,919 gallons (140 m^3) were applied, based upon hypolimnion alkalinity and volume, in 3 days (29-31 August 1975). Details are given in Cooke et al. (1978).

The alum applications had an immediate and dramatic effect on the total phosphorus content of the lakes, illustrated in Figure 8 for West and East Twin (the untreated reference lake). West Twin has continued to have low P content and improved water transparency through summer, 1980. Dollar Lake responded similarly (Figure 9), and hypolimnetic concentration in it has remained low 4 years after treatment, although not as low in 1978 as in 1976 (Cooke, 1979). The effectiveness of the floc may be beginning to decline in Dollar Lake.

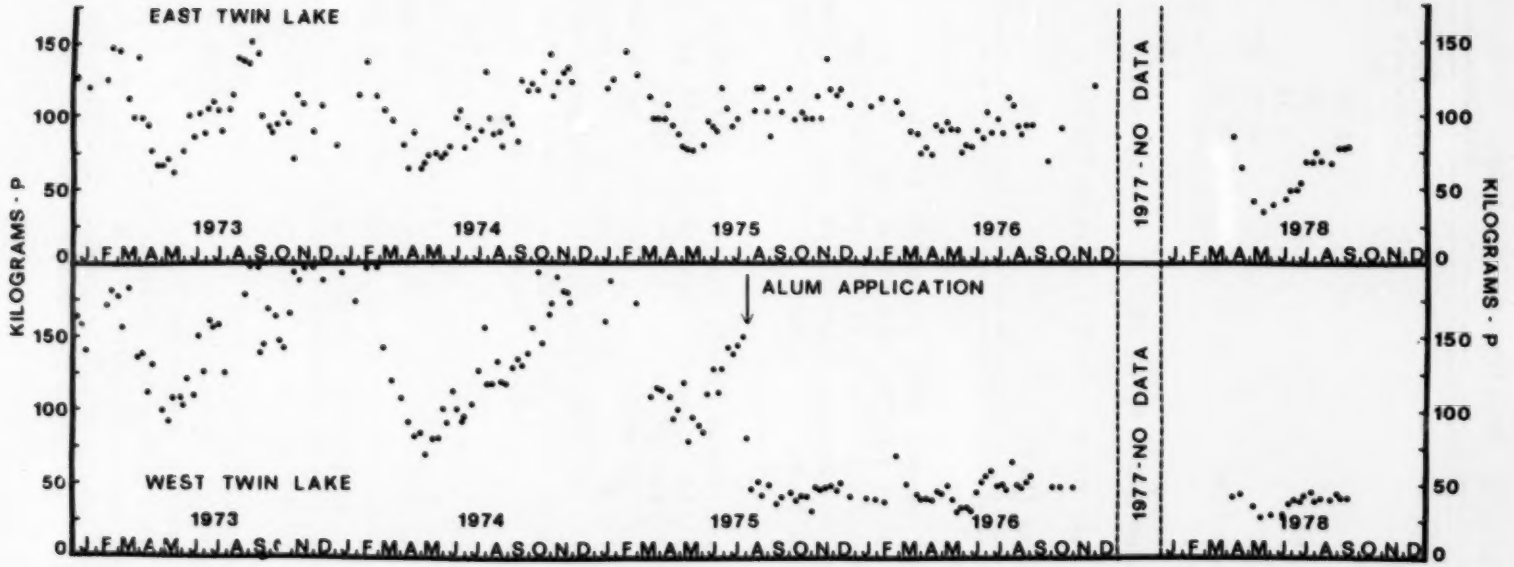
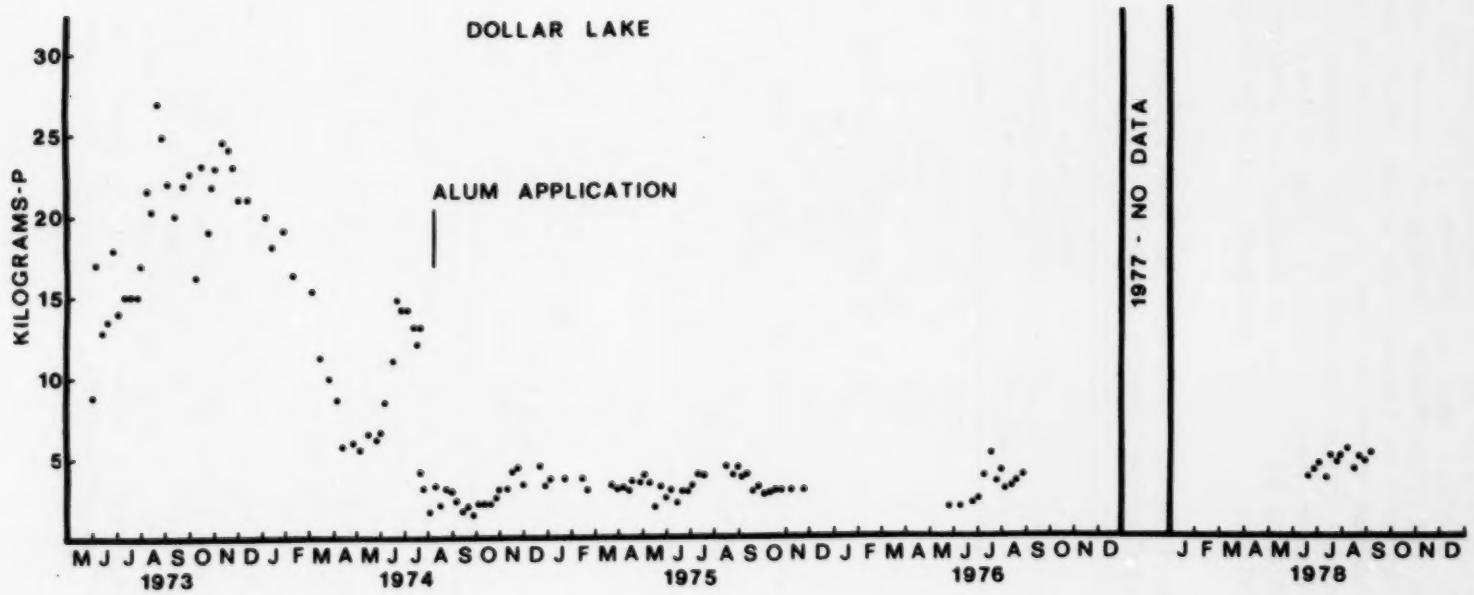


Figure 8. Phosphorus content (kilograms P) of East and West Twin Lakes. No samples in 1977 (from Cooke, 1979).


DOLLAR LAKE
KILOGRAMS-P
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ALUM APPLICATION
1977 - NO DATA
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1973
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1976
1978

Figure 9. Phosphorus content (kilograms P) of Dollar Lake. No samples in 1977 (from Cooke, 1979).

Internal P release was not completely controlled in West Twin (Table 4). Cooke et al. (1978), Cook and Kennedy (1977, 1978) and Cooke (1979) believe that unknown but significant internal P sources were in the littoral zone, since they had earlier (Kennedy and Cooke, 1974; Kennedy, 1978) demonstrated that the aluminum hydroxide floc was effective in controlling most of the P release from the treated sediments. This suggests that alum treatment will be more effective in lakes without a large littoral area or that the littoral area will have to be treated in conjunction with the hypolimnion. Unfortunately, a floc over littoral sediments could be unstable in wave-swept areas.

Table 4. Net External, Internal and Total Phosphorus Income to the Twin Lakes (mg $P/m^2/day$) During Summer

West Twin				
Year	External	Internal	Total	Days
1972	0.200	2.007	2.207	126
1973	-0.127	2.668	2.541	126
1974	0.435	0.831	1.226	116
1975	-------- No Calculation -- Alum Application --------			
1976	0.637	0.689	1.326	77
1978	0.334	0.163	0.497	101

East Twin				
Year	External	Internal	Total	Days
1972	-0.054	2.917	2.863	98
1973	0.207	2.804	3.011	112
1974	0.336	0.750	1.086	125
1975	-------- No Calculation -- Alum Application --------			
1976	0.663	1.022	1.685	72
1978	0.161	1.351	1.512	101

Note: 1. Negative external income due to negative groundwater income.
2. Days of summer defined as date of spring low phosphorus content to summer high phosphorus content. This interval corresponds to date of thermal stratification in spring and to beginning of destratification in fall.
(from Cooke, 1978).

Blue-green dominance was reduced in West Twin to about 80%, but East Twin, the downstream untreated lake, exhibited a much greater reduction (to 30% by 1978) in blue-green dominance. In both lakes total cell volume declined dramatically after the alum treatment, and the importance of greens, diatoms, and dinoflagellates increased. Very similar changes were noted in Dollar Lake (Kennedy, 1978; Cooke, 1979).

Changes in the Carlson Trophic State Index (Carlson, 1977), an index based on algal biomass, are listed in Table 5. The index is scaled so that each change of 10 units (e.g., 40 to 50) represents a doubling (or halving) of algal biomass. Total phosphorus changes are the best illustrators of change in trophic state due to the heavy use of herbicides and algicides in the Twin Lakes in the early 1970s, which temporarily increased transparency and decreased chlorophyll. Thus, Dollar Lake has had a 3-fold decrease in algal biomass and West Twin a 2.4-fold decrease 4 and 3 years after the aluminum sulfate treatments, respectively, and the lakes are now mesotrophic (a TSI value between 41 and 51 is usually found in mesotrophic lakes). The downstream untreated lake, East Twin, changed little from 1975 to 1976 but is now also mesotrophic due to the income of nutrient-poor water from West Twin.

An important side-effect was noted in 1979. After three years of increased water clarity the biomass and outward distibution of macrophytes from the shore has increased.

A significant increase in the number of planktonic microcrustacea species and Shannon H' (Shannon and Weaver, 1949) diversity occurred in West Twin, and these measures of community structure have remained significantly lower than East Twin through 1978 (Moffett, 1979). The dominant species also shifted from Cladocera to Copepoda. Since no residual dissolved aluminum was observed in the water column after treatment, it is speculated that these changes in community structure may be due to low pH or high aluminum in sediments where resting stages of these invertebrates may be found, or to the shift in the phytoplankton from blue-green dominance to diatoms and green algae, a change which may favor herbivorous copepods according to McNaught (1975). A higher copepod-cladoceran ratio is found in less eutrophic water (Gannon and Stemberger, 1978). The long term implications of the shift are not known. To date the treatment and these changes in pelagic zooplankton appear not to have been detrimental to sport fishing.

3. Medical Lake, Washington

Medical Lake, near Spokane, Washington (see Table 6 for features), maintained eutrophic conditions (algal mats, dissolved oxygen depletion) through internal recycling of nutrients from decomposing algae and from anaerobic sediments. It receives no surface water but presumably became enriched from groundwater flows which were contaminated by septic fields. This lake appeared to be ideal for an aluminum sulfate treatment since it is a seepage lake with a long water residence time and small littoral area. However, the alkalinity of the water is very high (about 750 mg/l as $CaCO_3$) and jar tests revealed that large doses would be required for P removal from the water column. It was determined from laboratory tests that multiple treatments and a combination of surface and hypolimnetic applications could be more effective than a single surface application for removal of phosphorus. During the 41 day period from 3 August to 13 September 1977, 936 metric tons of liquid alum (12.2 g Al/m^3) were added to Medical Lake for the purpose of P removal. There were 7 entire treatments of the hypolimnion and 4 at the surface. The application equipment was essentially the same as described for other lake treatments (Gasperino and Solter, 1978).

Table 5. Mean (May-September) Carlson Trophic State Index (calculated from surface measurements)

	West Twin TSI Values			East Twin TSI Values			Dollar TSI Values		
	Trans	Chl	TP	Trans	Chl	TP	Trans	Chl	TP
1968	-------- No Data --------			-------- No Data --------			-------- No Data --------		
1969	50.00			51.61					
1971	61.05	68.10	57.58	50.44	56.34	53.68	-------- No Data --------		
1972	48.30	57.94	62.75	52.78	60.27	58.91	-------- No Data --------		
1973	43.17	52.77	61.36	48.96	56.96	56.48	63.77	66.92	64.31
1974	49.86	60.56	59.84	50.51	58.24	58.89	See Kennedy (1978)		
1975	51.44	58.58	55.85	51.93	62.30	57.14	50.68	54.26	50.22
1976	46.72	49.78	52.36	51.44	52.40	56.62	47.94	53.23	50.65
1978	46.38	49.89	44.25	45.51	49.70	47.27	47.75	51.80	47.79
1971-1974	50.48	59.84	60.38	50.86	57.95	56.99	63.77*	66.92*	64.31*
1976-1978	46.55	49.84	48.31	48.48	51.05	51.95	48.79**	53.10**	49.55**
Decrease in Algal Biomass 1971-74 vs. 1978	0.79	2.00	2.41	0.48	1.38	1.01	3.00	2.76	2.95

* = 1973 data only.
** = 1975-1978 data.

(from Cooke, 1978)

Table 6. Physical-Chemical Data for Medical Lake*

Location:	25 km Southwest of Spokane, Washington
Watershed Area:	Closed Basin
Lake Area:	64 ha
Maximum Depth:	18 m
Mean Depth:	10 m
Volume:	6.07×10^6 m^3
Water Residence Line:	Unknown
Thermal History:	dimictic
pH Range:	8.5-9.5
Alkalinity (mg/l as $CaCO_3$):	750

* From Gasperino and Soltero (1978, 1979).

Total and ortho-P in the water column were lowered after fall turnover in 1977, a response similar to Horseshoe Lake (J. O. Peterson et al., 1973) and Annabessacook Lake (Dominie, 1978). The cause of this delayed response is not known. Concentrations of P fractions have remained low to date.

Before treatment, dissolved oxygen conditions in the lake were extremely poor and the lake did not support a fishery. After treatment, conditions improved greatly with no anoxic periods during ice cover in 1978 and 1979, and summer 1978 oxygen depletion occurred only a depths below 10 m. The lake now supports a rainbow trout fishery. The growth rate and condition factor of fish in Medical Lake exceeds that of most surrounding lakes (Gasperino and Soltero, pers. comm.).

Associated with improved oxygen conditions was an increase in transparency, decrease in chlorophyll, and a shift in the phytoplankton community from an assemblage of species dominated by blue-greens to a more diverse one with greens and flagellates. The phytoplankton became P-limited, as indicated by an algal bioassay. No negative impacts on the biota were observed despite an increase in dissolved aluminum to 700 µg Al/l during treatment. Current aluminum levels are 30-50 µg Al/l and are equal to the pretreatment concentrations (Gasperino and Soltero, pers. comm.).

The Medical Lake experience indicates that applicators may extend the period of treatment over many days and this could constitute a significant savings in labor costs.

4. Annabessacook Lake, Maine

The aluminum application to Annabessacook Lake illustrates the use of phosphorus inactivation/precipitation to control algal blooms in soft water. The nutrient budget methods of Cooke et al. (1977) was used by Dominie (1978) to demonstrate that 85% of summer P increase in this soft water (alkalinity = 20 mg/l as $CaCO_3$) lake was due to internal P release, presumably from sediments. The objective of the treatment was to control this P source. In order to maintain pH at near normal levels and thereby also prevent the appearance

of dissolved aluminum when aluminum salts were added, a mixture of aluminum sulfate and sodium aluminate, in a ratio of 1:1.6 was added to the hypolimnion of the lake in August, 1978. This ratio was determined empirically from jar tests to give good removal and little pH shift. This technique for soft waters was apparently first utilized at Snake and Long Lakes, Wisconsin in 1972 (R. Narf and T. Wirth, pers. comm.).

Annabessacook Lake has a surface area of 575 hectare and a hypolimnion area of 130 ha. The entire hypolimnetic area was treated in August, 1978, with the 8-10 m contour receiving a dose of 25 g Al/m^3, and the 10 m contour and below a dose of 35 g Al/m^3, using application procedures similar to earlier hypolimnetic treatments (Dominie, 1978; Dominie, pers. comm.). Had aluminum sulfate been used alone, the total dosage possible before dissolved aluminum approached the 50 µg Al/l level set by Cooke et al. (1978) would have been only about 4 g Al/m^3 (using the empirical dose relationships for West Twin and assuming that Annabessacook waters had similar properties to it), a dose which would not exert long-term control of P release.

There was little immediate P reduction at Annabessacook after the applications, as was found at Horseshoe and Medical Lakes, and it was not until September that a large decline in the lake's P content was observed. The treatment appeared to be successful in that pH shifts were minimal, no dissolved aluminum could be detected, and no adverse side effects were observed (Dominie, pers. comm.).

5. Braidwood Lagoons, New South Wales

All previous descriptions of the P inactivation/precipitation technique have been about lakes. May (1974) has reported the successful use of liquid alum and blocks of ferric alum ($Fe_2(S)_4)_3 \cdot 24\ H_2O$) in a shallow (max. depth 1 m) pond which had experienced severe blooms of toxic blue-green algae. The objective was to stop P release from anaerobic sediments by applying the chemicals to the pond surface, first in mid-winter (July 1971) and by adding the ferric alum at quarterly intervals as groups of suspended blocks (508 kg) which were replaced as they dissolved. A total of 1,067 kg of alum (10.60 g Al/m^3) and 2,540 kg ferric alum (31 g Fe/m^3) were added.

The pond's pH ranged from 5.0-5.5, phosphorus concentration remained low, and blooms of Anacystis cyanea and Anabaena circinalis did not occur during the subsequent summer. Monitoring ended in 1972.

6. Cline's Pond, Oregon

Lanthanum rare earth chlorides and zirconium were investigated by S. A. Peterson et al. (1974, 1976) for their effectiveness in P removal and for their toxicity. While lanthanum proved to be unacceptably toxic, zirconium, in doses ranging from 0.5 to 10 mg Zr/l in a static bioassay, was non-toxic to Coho salmon for up to 10 days of exposure but did exert small chronic mortality and impairment of reproduction in Daphnia magna. This lead the authors to conclude that while zirconium was as much as 3.5 times more efficient than aluminum in removing P from pond water, further experiments were needed before zironcium could be used by the public.

Powers et al. (1975) continued the work of S. A. Peterson et al. by a pilot scale test of the effectiveness of zirconium chloride addition in removing P. On 26-27 March 1974, a dose of 5 g Zr/m^3, buffered with NaOH to counteract the pronounced pH drop produced by hydrolysis of $ZrCl_4$, was added to half of Cline's Pond (0.5 ha), after dividing the pond with a polypropylene curtain.

A bloom of Anabaena circinalis developed on the control side in July, but the treated side was clear, with 5 times less chlorophyll a and 2.5 times less P. Their data suggest that Zr inhibited recycling of P from the sediments and that the treatment was not toxic to algae but made them P-limited. Kumar and Rai (1978), in laboratory studies with Chlorella, also noted that inhibition of growth was due to P-limitation and not toxicity of $ZrOCl_4$. Macrophytes spread over one-third of the experimental area of Cline's Pond. This was attributed to the greatly increased water clarity.

The Cline's Pond and the Braidwood Lagoon experiments illustrate the efficacy of P inactivation/precipitation in smaller systems, and the use of inactivants other than aluminum. At present, the cost of zirconium is high and it is not generally available.

7. Wahnbach Reservoir, Germany

Bernhardt et al. (1971) and Bernhardt (1978, personal communication) describe a special use of phosphorus precipitation to improve the quality of water entering the drinking water treatment plant at Wahnbach Reservoir. After impoundment in 1957, the reservoir was very eutrophic, with blooms of Oscillatoria rubescens, and treatment for drinking purposes became costly and increasingly difficult. Since the primary sources of nutrients were non-point, it was decided to allow water to flow into a pre-reservoir, precipitate P, flocculate and filter this water, and then allow it to flow into the main reservoir. The treatment plant was completed in 1977 and treats income to the pre-reservoir up to 8 m^3/sec without flooding. Pumps, operating at 18,000 m^3/hr, lift water out of the reservoir and P is precipitated with Fe^{+3}, and the iron phosphate is then removed by flocculation with alum. Negatively charged particles and colloids are destabilized, the floc agglomerated, treated with a polyelectrolyte, and then filtered. Total P concentrations in the emerging water averages 4 µg P/l, a 95% reduction. Plankton development in the reseroir has become much less.

V. Costs for Phosphorus Inactivation/Precipitation

Funk and Gibbons (1979) have summarized the costs for materials, supplies, transportation, construction, and application for four lakes. Their summary indicates high cost variability among treatments, in part due to changing prices of labor and chemicals.

The most expensive portion of phosphorus precipitation/inactivation may be labor. Labor costs (expressed as man-days or one person working 8 hours) for several aluminum treatments are summarized in Table 7 along with dose and area tested. Few relationships appear from these data, due primarily to the low doses and surface treatments of Horseshoe and Liberty Lakes and the

Welland Canal. If these three are omitted, there appears to be a curvilinear relationship between area treated and man-days. There was a difference of only 6 man-days labor for application between the surface-hypolimnetic treatment of Medical Lake (64 ha treated) and the hypolimnetic treatment of Annabessacook (121 ha treated), but a difference of 56 man-days between the 16 ha hypolimnetic treatment of West Twin and Medical Lake.

More data are needed before a quantitative relationship between treatment area and man-days can be stated. For planning purposes, persons considering a hypolimnetic treatment designed to control P release will find that labor costs for application will be higher for small treatment areas. The cost of construction could be offset because application vehicles can be used for subsequent treatments of other lakes or modified for other purposes.

Table 7. Dose, Area Treated, and Man-Days for Application of Aluminum Salts

Lake	Dose g Al/m^3	Area Treated (ha)	Man-Days for* Application	Kilograms Al	Man-Days/ ha
1. Horseshoe	2.1	8.9	11.8	946	1.33
2. Welland Canal	2.5	74.0	100.0	15,490	1.35
3. Dollar	20.9	1.39	6.0	1,797	4.3
4. West Twin	26.1	16.0	73.8	8,649	4.61
5. Liberty	0.5	277.0	36.0	95,300	0.13
6. Medical	12.2	64.0	130.0	75,853	2.03
7. Annabessacook	-30**	121.4	136.0	11,654	1.12

* 1 person working 8 hours (note: most treatments were done with 12-14 hours working days, increasing labor costs but also increasing efficiency).

** Different doses were given to shallow and deep hypolimnetic waters.

VI. Summary

1. The purpose of the phosphorus inactivation/precipitation technique for lake rehabilitation is to lower the phosphorus concentration in the water column. The expected result is an increase in transparency, fewer algae, and increased recreational potential. Aluminum has been the inactivant/precipitant of choice to date.

2. The technique is effective in removing inorganic (precipitation) and particulate (entrapment) P from the water column, thereby bringing about an immediate decrease in algal blooms and an increase in transparency. If sufficient aluminum hydroxide floc is formed over the sediments, P release during anaerobic conditions is retarded and long-term control of P concentration in the water columns may be achieved (at least 5 years) if there has been nutrient diversion. Treated lakes have promptly changed from a "eutrophic" to

a "mesotrophic" classification and have remained in that state for at least 5 years after a sediment treatment to control P release. Ponds can be effectively treated also.

3. Some lake treatments with aluminum have been ineffective or have had short-term effectiveness only. Failures can usually be traced to incomplete nutrient diversion and to insufficient dose.

Lakes with large littoral areas may continue to have higher P concentration than expected after an open water application due to P generation from littoral sediments by macrophytes, animals, and groundwater. This apparently cannot be halted by an aluminum application to littoral sediments, except perhaps for internal P "loading" brought about by flow of groundwater through P-rich littoral sediments.

Lake treatment will not be effective if nutrient diversion is insufficient, or if there is rapid flow-through of water. In both of these instances, as well as with "internal P loading," a water-P budget is needed to assess their significance before application.

In some cases the dose of aluminum has been adequate to remove P from the water column but too low to affect lasting control of P release from sediment. The amount of aluminum hydroxide needed to achieve such control is unknown but it will usually be in excess of the amount needed for P removal.

4. Persons contemplating an aluminum application should address these pertinent problems:

a. How much aluminum should be added? An answer to this is not now clear but it appears that a dose in excess of an Al:P molar ratio (but not to exceed toxic levels of 50 µg Al/l), as determined from jar tests is required for control of P release. Monitoring data are scarce, and nearly all high-dose lakes have been treated in 1977-78, so that the relation between dose and duration of effect is unknown. In the West Twin-Dollar Lakes experiences, the only lakes for which there is any published long-term monitoring, effective P control was maintained for at least 5 years with doses over 20 g Al/m^3.

b. What area of the lake should be treated? At a minimum, the area of anaerobic sediments should be covered with floc.

c. Will there be unacceptable side effects? Experience to date indicates that as long as pH remains in an acceptable range and residual dissolved aluminum does not exceed 50 µg Al/l, there will be no toxic effects to fish. There is evidence of significant reduction in the species diversity of planktonic microcrustacea. Increased water clarity may stimulate macrophyte growth, particularly in ponds and shallow lakes.

5. Unit cost for treatment has not been established, but is related to area and to amount to be added. For those treatments for which detailed costs have been published, the mean (N = 5) man-days/metric ton applied is (± s.e.) 10.8 ± 4.83, for actual application. Construction, monitoring, and cleanup will be additional.

There is apparently no significant social impact with phosphorus precipitation/inactivation since disruption of lake use is minimal. There are no disposal problems and no restriction on subsequent water use.

6. There are a considerable number of gaps in our knowledge about this restoration technique. The relationship between dose and longevity of control is poorly known. Only a few treatments have had sustained monitoring to assess effectiveness and side-effects. A number of questions remain. How often is reapplication necessary? Is a surface application as effective as a hypolimnetic one in controlling P release? More toxicity studies, directed primarily towards the actual level of organization to which the aluminum is applied rather than to species, are also needed. What effect would an early spring littoral application have on subsequent summer growth of macrophytes and internal P release from the littoral?

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